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Vapor Pressure Determinations
By the Saturation Method

Chemical Engineering

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VAPOR PRESSURE DETERMINATIONS
BY THE SATURATION METHOD

BY

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THESIS

For the Degree of Bachelor of Science

in Chemical Engineering

College of Science

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Drury Lee Weatherhead

ENTITLED Vapor Pressure Determinations by the

Saturation Method.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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INTRODUCTION AND HISTORICAL PART.

The great experimental difficulties that attend the determination of the vapor pressure of solutions have prohibited the collection of much data in this line. The chief difficulties have been due to the lack of suitable apparatus, several forms of which have been used without very good satisfaction.

The "static" method was the first to give any degree of satisfaction. A tube open at one end is filled with mercury and inverted so that its mouth is in a mercury well, open to the atmosphere. Some of the solution or solid to be experimented on is introduced into this tube and from the fall in the mercury level the vapor pressure is calculated. This method which has been experimented with by Moser,⁽¹⁾ Magnus,⁽²⁾ Wüllner,⁽³⁾ Raoult,⁽⁴⁾ and others is very simple, but is open to several objections. Tamman⁽⁵⁾ has shown that small quantities of air and impurities greatly influence the results. The liquid in the tube may not remain at a uniform concentration, which is a necessary condition to obtain accurate results. Drops of liquid on the sides of the tube cause a decrease in pressure and introduce an ap-

preciable error.

Ramsay and Young⁽⁶⁾ used an indirect method which consists in measuring the temperature of a boiling solution under varying pressures. Emden⁽⁷⁾ also used this method. It is open to the following serious objections, however: the superheating of the solution and vapor, the change in concentration of the boiling solution due to vaporization of some of the solvent, and the great change in the boiling point due to a small change in pressure. Also, since the solutions must be boiled, decomposition may take place in some cases and so vitiate the results. This method gives a very limited range for determinations. Dieterici⁽⁸⁾ and many others have used differential methods. The character of the operations outlined and the nature of the objections raised to these methods show that they are subject to considerable error and on the whole are not very satisfactory.

The "air bubbling" method has also been extensively used. The principles involved are the same as those of the "saturation" method, which will be used in these experiments. It is based on Dalton's law of partial pressures, namely; that in a mixture of gases the ratio of the pressure of any gas in the mixture to the total pressure is equal to the ratio of the volume of that gas to the total volume. Thus, in ordinary air, saturated with water vapor, the relation is

$$\frac{\text{Pressure of Water Vapor}}{\text{Total Pressure}} = \frac{\text{Volume of Water Vapor}}{\text{Total Volume}}$$

The volume of water vapor contained in a measured volume of air saturated with vapor is found by extracting the water from the air by passing it over a drying agent, and from the weight of water obtained, calculating the volume. Hence a value for the density of water vapor must be known. It is assumed to be normal as compared with oxygen, that is, General Gas Law must hold for water vapor and Dalton's law for air and water vapor.

Regnault⁽⁹⁾ first employed this method in 1845 and obtained values for the vapor pressure of water which are taken as standard at present. His method of procedure was as follows: Air was passed through a flask containing a sponge moistened with water and then through a second flask containing sheets of silk, moistened with water, so arranged that the air had to penetrate them. The air was then dried in absorption bulbs and led into an aspirator where its volume was measured. The data so collected gave values agreeing closely with results from the "static" method.

Tammann⁽¹⁰⁾ recalculated Regnault's results from the data as he gave them. There were discrepancies for which Tammann could find no reason. He also employed this method in determining the vapor pressures for several hydrates and solutions; the values agreeing very well with those obtained by the static method. The formula by which his calculations were made is given below:

$$f = \frac{H}{1 + \frac{V_0(1 + kt')}{P(1 + at')} \frac{Wd}{760} (H - f')}$$

Where

t = the mean temperature of air saturated with water vapor

f = the vapor pressure of water at the temperature of the experiment, t .

t' = temperature of the aspirator at end of experiment

f' = the vapor pressure of water vapor at the temperature t'

H = the height of barometer reduced to 0° C. at close of experiment

a = the coefficient of expansion of air = .003671

k = " " " " " the material of the aspirator.

V_0 = the volume of the aspirator at 0° C.

W = the absolute weight of a liter of air at 0° C. theoretical

d = the density of water vapor

$$Wd = 0.8042 \text{ g.}$$

P = weight of water absorbed.

About the same time that Tammann did his work Shaw⁽¹³⁾ investigated the methods of determining the hygrometric condition of the air. He used the "air bubbling" method to determine the moisture in the air, obtaining very satisfactory results. His calculations were made by the following formula, based on the same principles as those of Regnault and Tammann, but arrived at in a little different way:

$$e = X \frac{W}{V} \left(1 + \frac{E - X \frac{W}{V}}{B} \right)$$

Where

e = pressure of aqueous vapor

X = a constant $\frac{760(1 + aT)}{Dd}$

T = temperature of air in aspirator

E = pressure of water vapor at temperature T

B = height of barometer at same time

w = weight of absorbed moisture

V = volume of water that runs out of aspirator

a = coefficient of expansion of air .00366

D = density of air at 0° C. and 760 m.m.

d = sp. gr. of aqueous vapor referred to air
at the same pressure and temperature.

The derivation of this formula is shown in the article by Shaw referred to above. He also showed that weighing the absorbing tubes under different conditions of temperature and pressure might introduce an error amounting to a considerable fraction of a milligram, if the weight was not corrected to weight in vacuum each time. He used one U-tube filled with pieces of pumice stone saturated with sulphuric acid and then ignited, and one filled with layers of phosphorus pentoxide. His experiments showed conclusively that a set of two tubes dried the air perfectly. Regnault, Tammann, and Shaw all used a rather rapid rate of flow of the air. Shaw called attention to the fact that air saturated with moisture passing through a glass tube was apt to have considerable moisture deposited on the walls of the tube. If such a tube is heated to a degree or so above the temperature of the room, no condensation occurs.

Ostwald(11) modified Regnault's method. He passed air through two potash bulbs containing the solution and then through one containing pure water. In going through

the first bulbs the air became saturated up to the vapor pressure of the solution. In going through the water it became saturated up to the value for pure water. The air was then dried in absorbing tubes, their gain in weight obtained, as well as the loss in weight of the water. The loss in weight of the pure water and the gain in weight of the absorbing tubes were in the same relation as the difference in vapor pressure of the solution and of water, and the vapor pressure of pure water. Walker⁽¹²⁾ used this method for determining molecular weights in dilute solutions.

Carveth and Fowler⁽¹⁴⁾ aimed to devise a simple laboratory method for determining vapor pressure of solutions using the principles of Regnault's method. A serious objection to **that** method is the long time consumed in carrying out an experiment, due to the very slow rate of flow of the air.

Perran⁽¹⁵⁾ in his excellent work has conclusively shown that this slow rate of flow is not necessary. He concluded that air should not be drawn through faster than one-tenth liter per minute for high temperatures. He assumed that water has a normal density and that its specific volume is 1.242. The following formula by which he calculated his results depends upon the same factors as the other formulae; the difference being that he used the specific volume in place of the density:

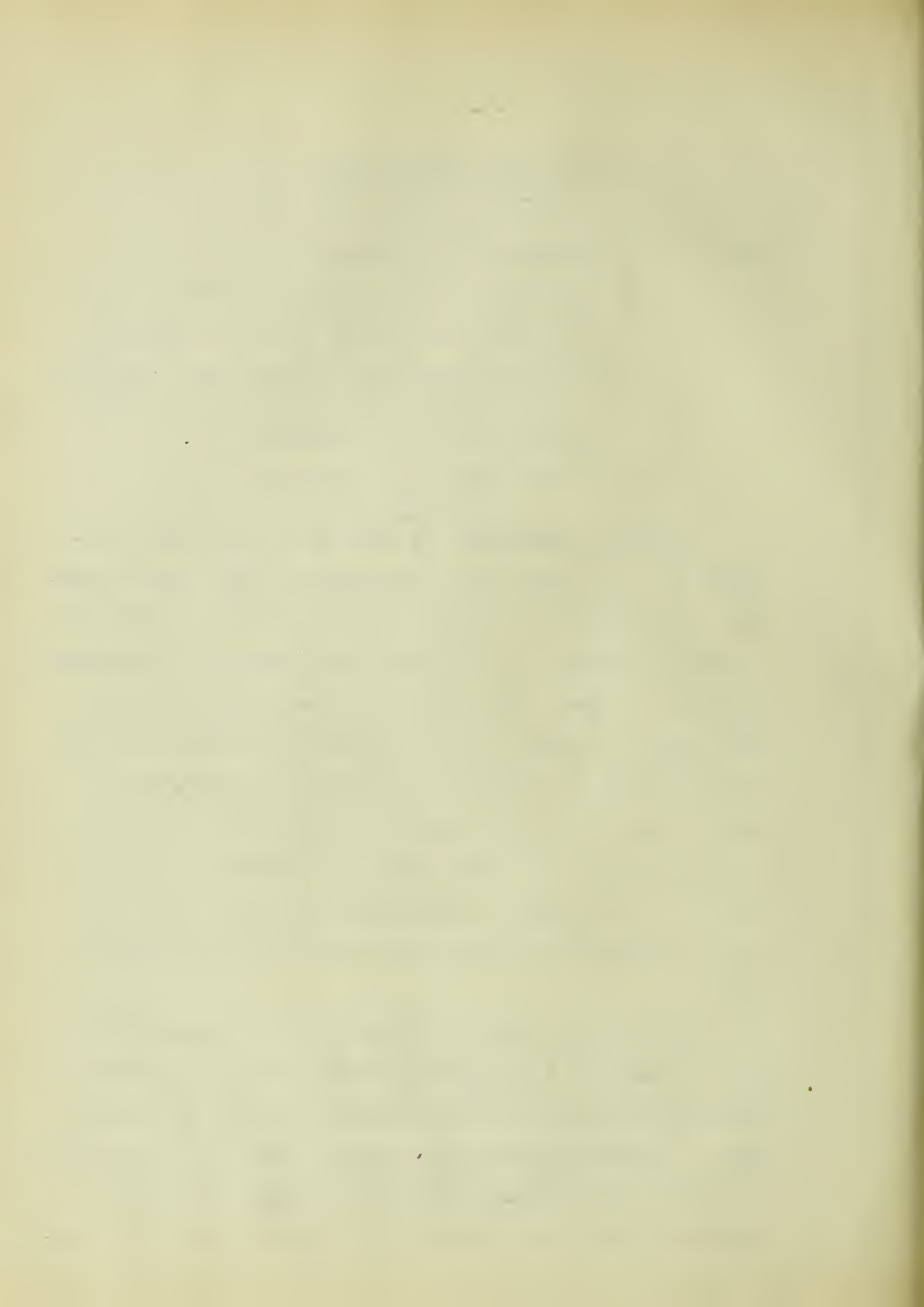
$$f = \frac{1.242 \times 760 \times W.P.T.}{T(1.242 \times 760W) + 273 \text{ W.p.}}$$

Where W = weight of water drawn off
 P = pressure in last aspiration flask
 T = absolute temperature of air in aspirator
 V = volume of air drawn through water, measured
 at temperature and pressure of aspirator
 p = pressure of air in aspirator
 f = vapor pressure of solution.

Perman

From his experiments **A** came to the following conclusions: "(1) When air is aspirated through water it becomes saturated with aqueous vapor with great rapidity. (2) In the saturated air so obtained, the pressure of the aqueous vapor is the same as the vapor pressure of water when no other gas is present. (3) The density of the aqueous vapor in the mixture is normal. (4) The density of saturated aqueous vapor (without admixture) is probably only very slightly, if at all, above normal at temperatures up to 90° C." He further called attention to the fact that the hygroscopicity of glass is a source of experimental error.

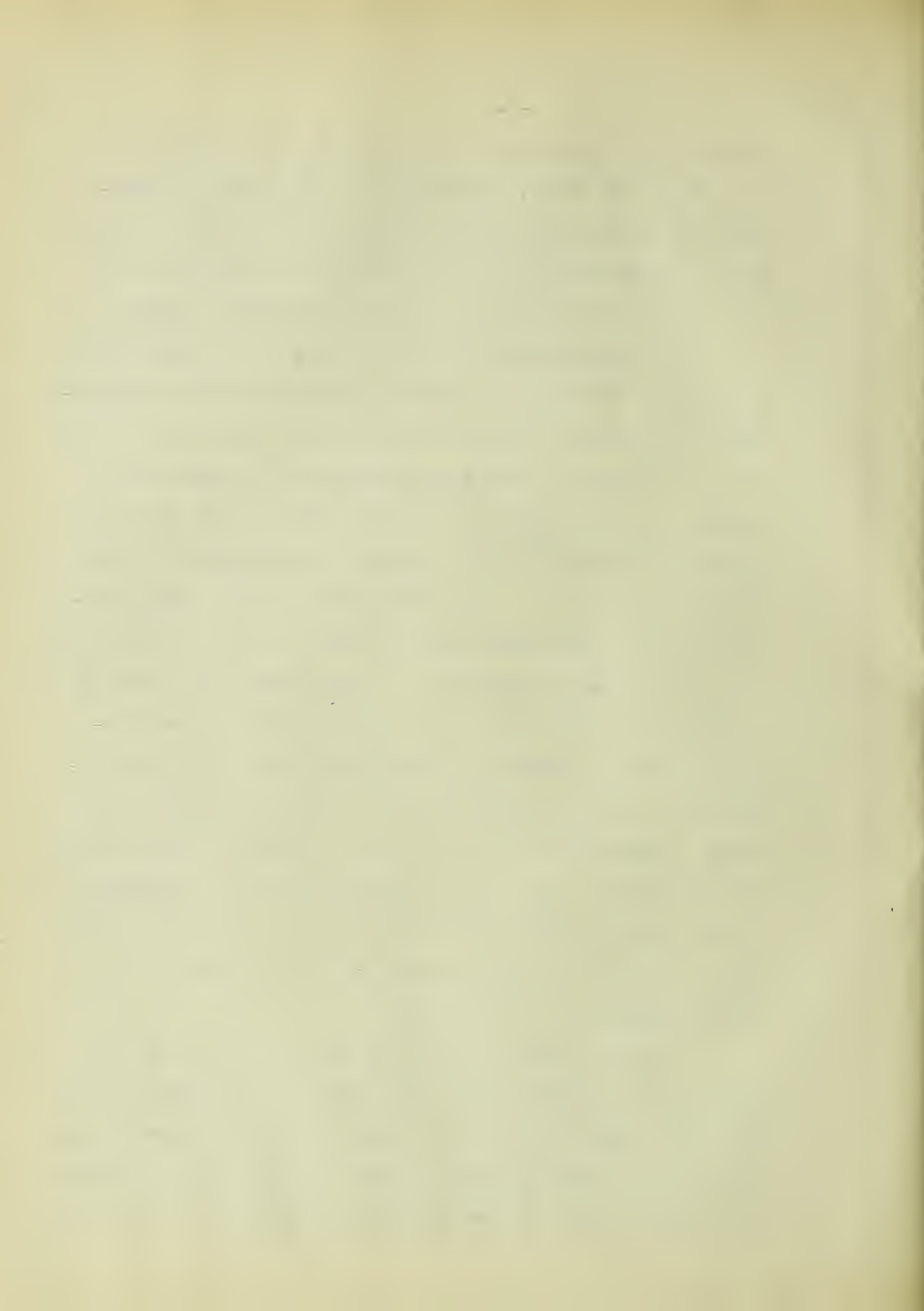
Mr. E. G. J. Hartley and the Earl of Berkeley⁽¹⁶⁾ used the method of Ostwald except that they arranged the apparatus so that the solution could be agitated and thus given a chance to thoroughly saturate the air. They changed the form of the saturating bulbs and placed them upon a platform which was so arranged that one end could be alter-



nately raised and lowered, thus sending the liquid from one end to the other, agitating it, and mixing it thoroughly with the air. This idea was put forth at the same time by Kahlenburg,⁽²⁰⁾ it being the first time that the liquid had been agitated in the "air bubbling" method.

This new feature made it possible to dispense with bubbling air through the solution so that the air was saturated by passing it over the highly agitated liquid. Thus the "air bubbling" method was changed to a "saturation" method. A. T. Lincoln and D. Klein⁽¹⁹⁾ first used the apparatus described in this paper in experiments on the "saturation" method. They found that the air became saturated when a reasonable rate of flow was used; four liters per hour proving satisfactory. Experiments were carried on to show that equilibrium was reached whether it was approached from a higher or lower temperature. It was demonstrated that the dry air entering the aspirator bottle became saturated with water vapor and reached equilibrium with the water by the time the experiment was completed. It was further proved that the solution in the saturation did not change in concentration due to the passage of a large quantity of air over it.

The main questions upon which there has been discussion in connection with the "saturation" method are as follows: Does Dalton's law apply in this instance? Does water vapor have a normal density? Does water vapor exert the same pressure in the presence of admixed air as in the



absence of any gas? Does air become saturated with water vapor rapidly enough to permit an experiment like this one to be accurate? Minor points which have to do with the apparatus have also been discussed and show the apparatus to work satisfactorily when due care is exercised. In his paper Ferman⁽¹⁵⁾ covered the main questions and showed the method to rest upon a sound basis. Chaw⁽¹³⁾ also drew conclusions in the same direction.

EXPERIMENTAL.

A general view of the apparatus used and its arrangement is shown in Plates I and II. Plate III gives a diagrammatic sketch of the train for purification and saturation of the air. In this diagram J' is a Drechsel bottle filled with pieces of pumice stone ~~and~~ saturated with sulphuric acid to remove ammonia from the air. J contains soda lime to remove carbon dioxide. I contains water to replace the moisture abstracted from the air by the sulphuric acid. H, G, F, and E are submerged in the bath. H is a Woulff's bottle containing pure water to increase the water content of the air. G is a lead coil ~~coil~~ about six feet long through which the air passes, to bring it to the temperature of the bath. F is a second Woulff's flask containing the solution under examination and is used to bring the air into equilibrium with the solution as nearly as possible

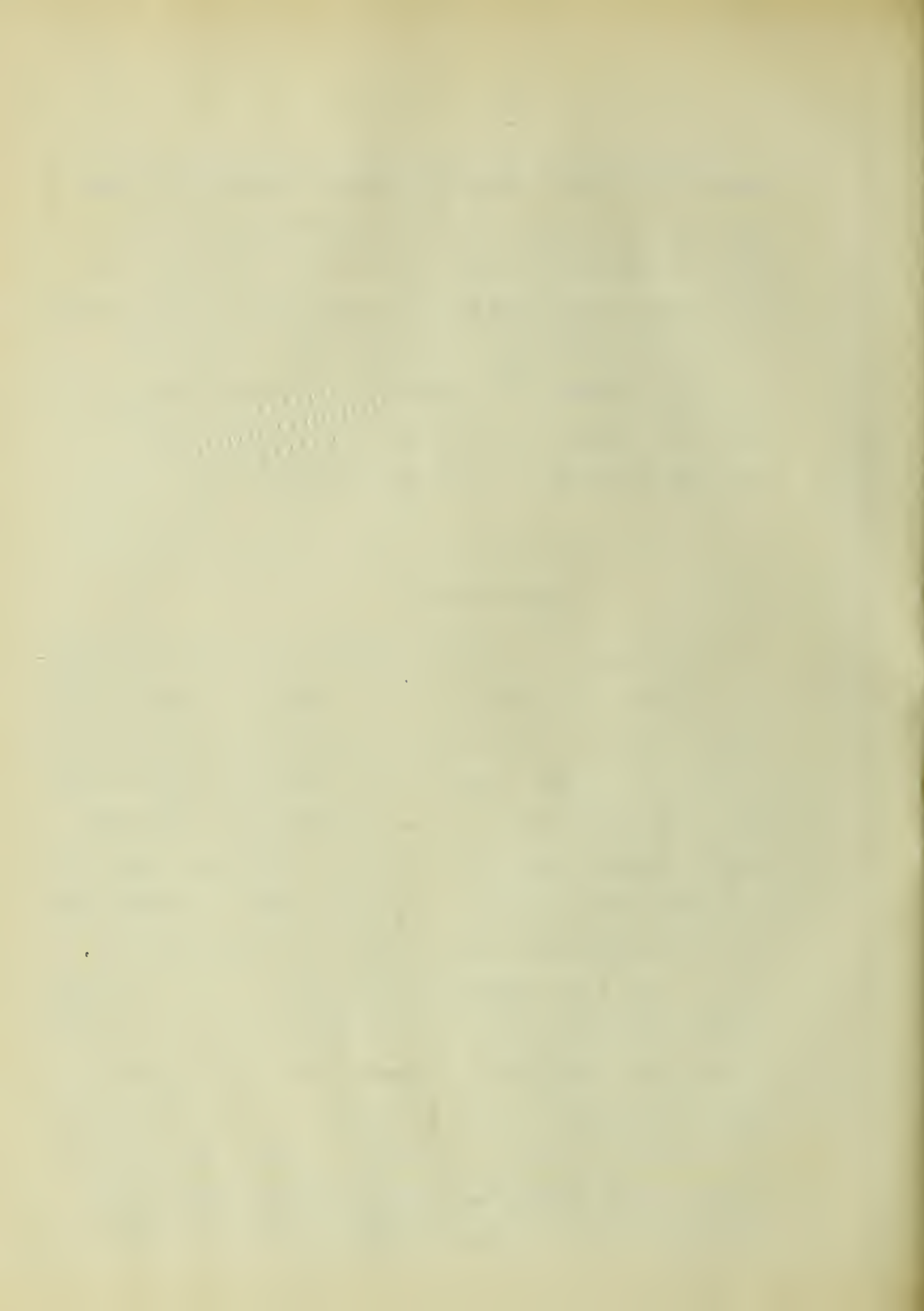
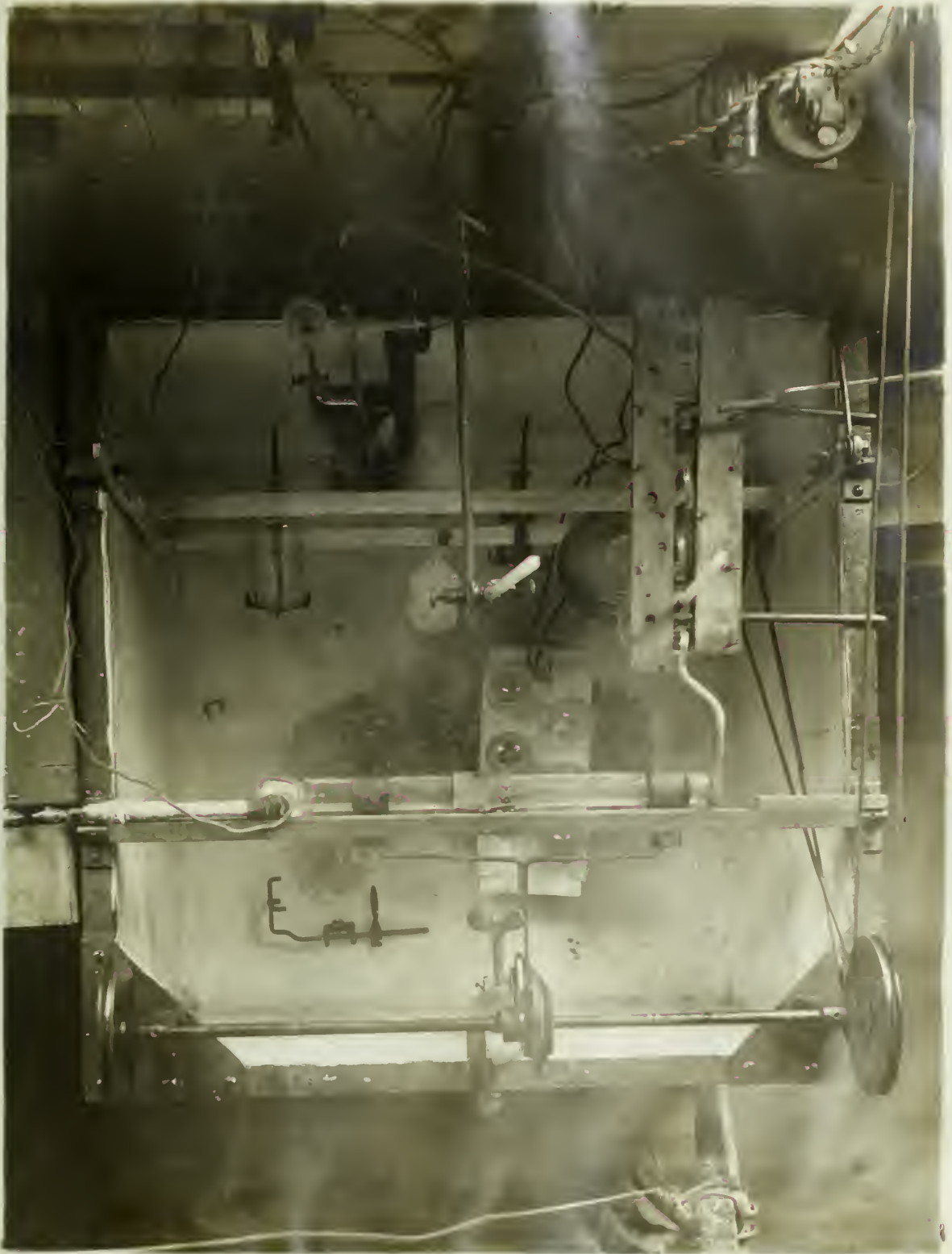


PLATE I

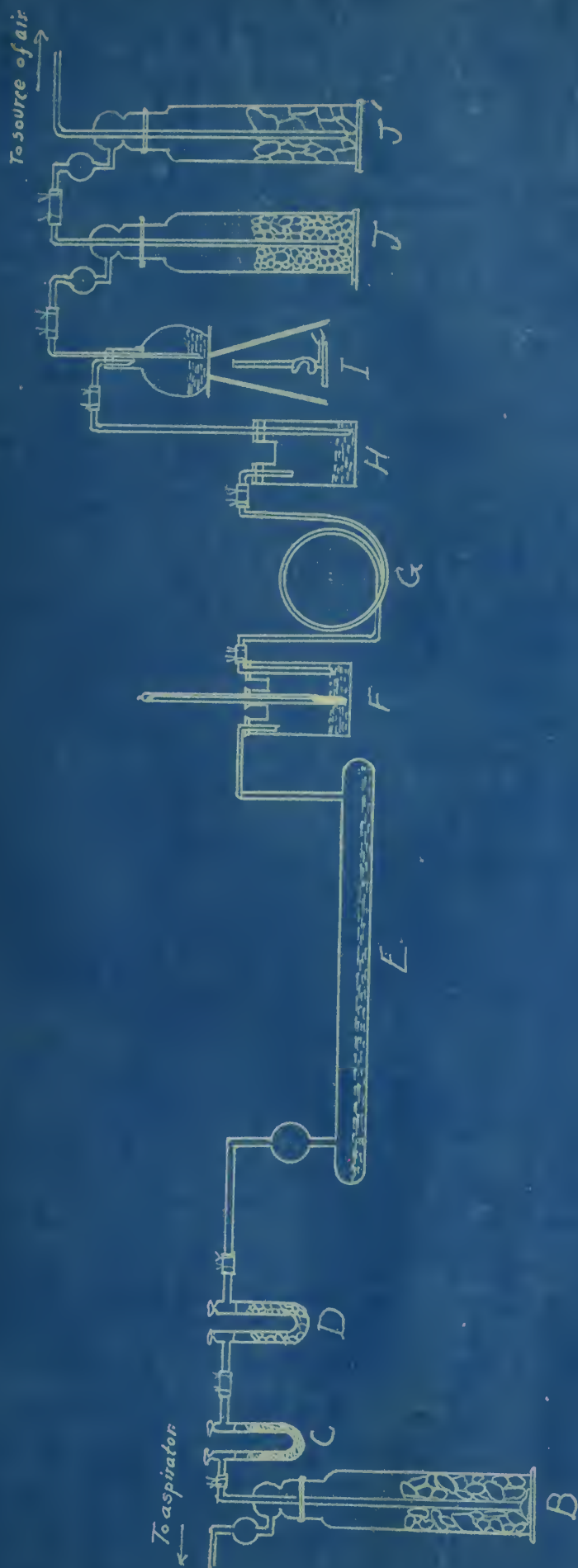


1872
1873

PLATE II



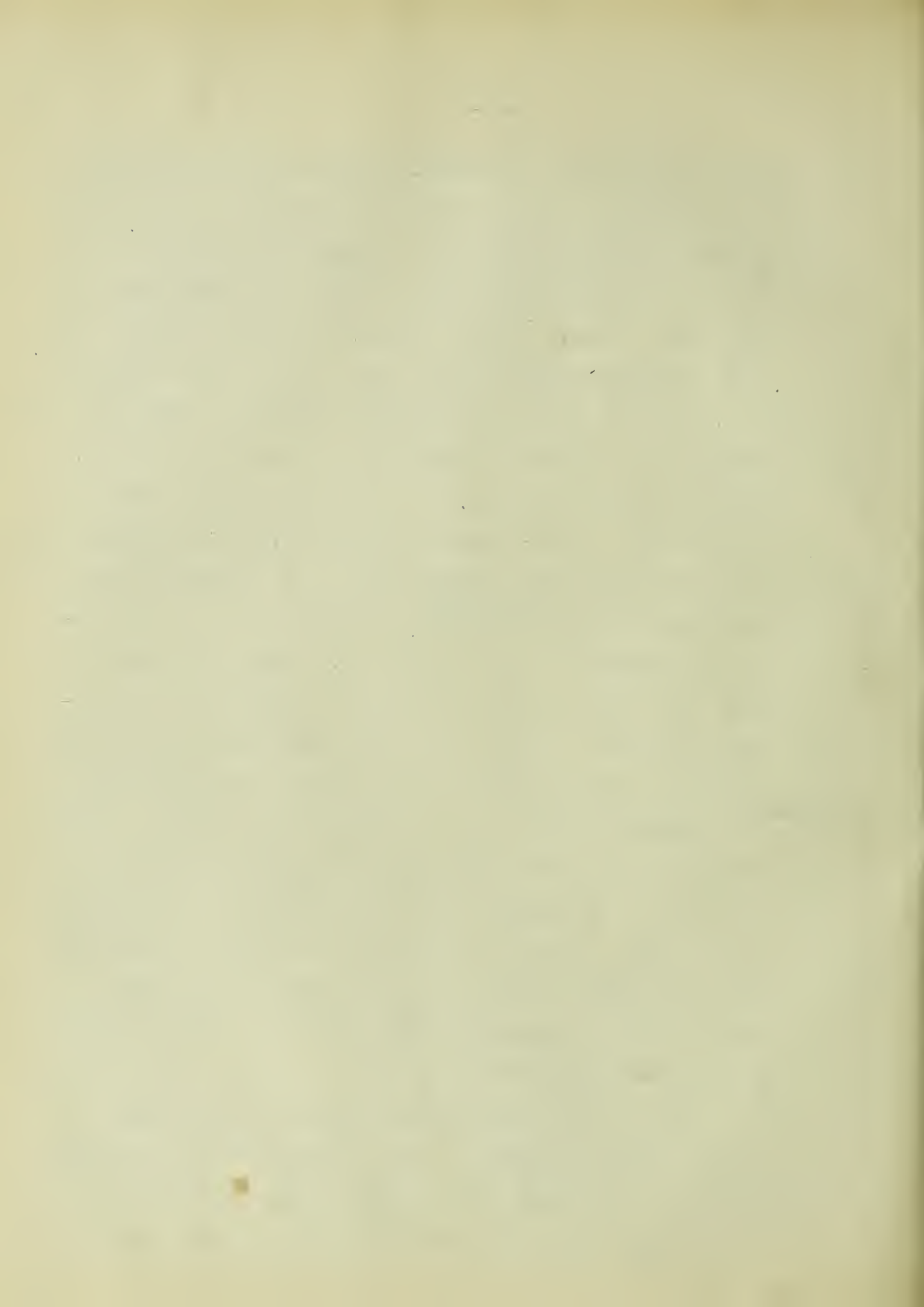
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before entering the saturator, so that the concentration of the solution in the saturator is changed as little as possible. The air next passes through the saturator. D is a U-tube of the Schwartz type with ground glass stop cocks. It *is* filled with small pieces of pumice stone saturated with sulphuric acid. C is a tube similar to D, except that it is filled with alternate layers of phosphorus pentoxide and glass wool. As mentioned before, Shaw has shown two such tubes to be a sufficient dryer for the air. B is a Drechsel bottle filled with pumice stone saturated with sulphuric acid. It prevents C from absorbing water vapor from the aspirator. One of the aspirator bottles is shown in Plate I. Two such bottles were used alternately as aspirator and receiver. The bottles were each of thirty two liters capacity and graduated in liters, the water levels being marked on the outside tube connected to the top and bottom of the bottle. These flasks were calibrated by drawing water from them into calibrated liter flasks and marking the water levels on the outside tube. These calibrations were checked by weighing the bottle full of water and then empty and also when partly filled. The weights were made on a platform scales weighing accurately to ten grams.

The general arrangement of these various parts of the apparatus about the tank is clearly shown in Plates I and II. The tank was of sheet iron, 30 in. x 30 in. x 25 in. deep, containing about 350 liters. The apparatus,

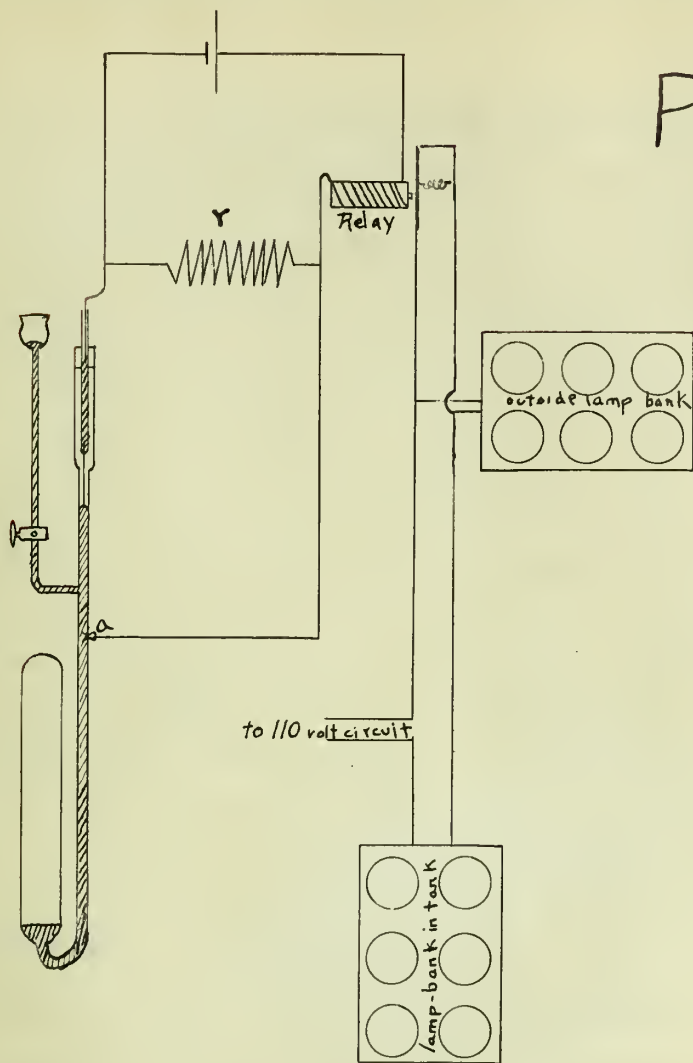


except for the thermo-regulator, is the same as used by Lincoln and Klein⁽¹⁹⁾ and described by them. The form of the thermo-regulator will be described in more detail.

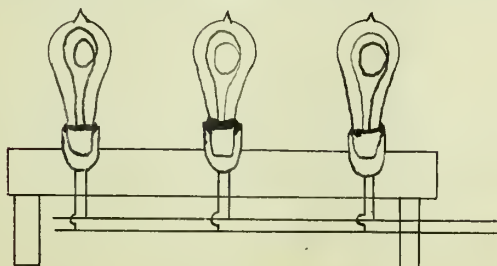
The regulator was an electric device somewhat like that used by Moise and Frazer⁽¹⁷⁾, similar to the one described by Geer⁽¹⁸⁾. A diagrammatic sketch of it is given in Plate IV. The thermometer part was very much like that part of the ordinary Ostwald gas regulator. The large tube was filled with toluene except at its bottom which contained mercury. The mercury extended up the tube and made contact with the platinum wire, sealed through a glass tube inserted in the cork in the top. A platinum wire was sealed into the smaller tube at a, from which a wire led through the coils of a relay to one pole of a battery. The other pole of the battery was connected to the platinum wire in the top of the tube; a small wire resistance, r , was placed in parallel with the thermometer part. This was to reduce sparking at the platinum contact when the circuit was made and broken. Thus, the current went through the relay coils all the time, but when the circuit through the thermometer was broken, the current was not strong enough to hold the relay open. The resistance used was as small as could be ~~used~~ without allowing enough current to go through the relay to keep it open all the time. This reduced sparking to a minimum. The relay controlled a 110 volt circuit running through two lamp banks of six, sixteen candle power lamps each. One bank was set on the

ARRANGEMENT OF HEATING DEVICE

PLATE IV



LAMP-BANK TO HEAT THE BATH



wall at a convenient place. The wires leading up to it are shown in Plate I, but the bank was too high to be included in the plates. The other bank was set on the bottom of the tank as in Plate II. This bank was made by setting lamp sockets such as are used on the incandescent lamp hung out of doors, into a block of wood and sealing them in with hot sealing wax. The leads from these sockets were soldered to two insulated wires as shown and the connections were well taped. Leakage of current through these connections was slight. The lamps were sealed into the sockets with sealing wax, which prevented short circuiting. The block was supported on legs at the corners and was weighted down by a block of lead. The regulator worked as follows: When the bath was at the desired temperature, the platinum wire was set to make contact with the mercury in the tube. This closed the relay circuit and opened the relay which opened the 110 volt circuit, thus putting the two lamp banks in series. The lamps in the water burned at half voltage and supplied about enough heat to make up for radiation. As the bath cooled below the desired temperature, the mercury in the tube fell and the relay circuit was broken. This opened the relay and closed the 110 volt circuit, short-circuiting the outside lamp bank and supplying full voltage to the lamps in the tank. With the bath in a room not subjected to strong air draughts and at ordinary temperature, a temperature varying $\pm 0.002^{\circ}$ C. read on a Beckman ther-

mometer, can be maintained throughout the duration of an experiment. A Bunsen burner was put under the tank to bring the bath up to the proper temperature before starting the electric heating device when the temperature was several degrees too low.

All thermometers used in these experiments could be read to 0.1° C. and estimated to 0.01° C. They were standardized against a thermometer reading to 0.05° C. which had been standardized at the Bureau of Standards at Washington, D. C. This standard thermometer was also used to give the temperature of the bath and a Beckman thermometer with the mercury set on a convenient part of the scale was used to give the exact temperature of the bath. All experiments were carried on at 25° C.

Experiments were first made on pure water to get the apparatus in good working order. As it has been shown that any grease in the saturator tube tends to make the results unreliable, the saturator was thoroughly cleaned with hot concentrated alkali, then with chromic acid and then steamed out with fat-free water. The water used for determinations and for solutions was made by distilling ordinary re-distilled water from potassium dichromate and sulphuric acid, sending the steam through barium hydrate solution and condensing it in a block tin condenser. This water was fat-free and contained only 0.01 part per million ammonia.

The concentrations of the various solutions were



found by evaporating a weighed portion to dryness in a platinum dish. This method was checked by ammonia determinations by both Kjeldahl's and Folin's methods.

If any salt were to collect in the tube leading from the saturator, it would be apt to take water from the air if it were hygroscopic. Some of it might be taken over mechanically by the air. As this affects the results, care was taken to keep the tube free from solution and salt. The tube leading from the saturator to the absorbing tubes was heated two or three degrees above room temperature by a platinum wire through which an electric current passed, to prevent condensation of moisture in the tube and loss of water vapor.

A rate of about four liters per hour was used in aspiration, a rate not in excess of that used by Regnault, Shaw and Tammann. The temperature of the air in the aspirator was taken at the completion of the run in all cases. The apparatus was driven by a 110 volt, one-sixth horse power motor. The saturator was given about 250 oscillations per minute and the stirrer about 75 revolutions per minute. The barometer readings were corrected to 0° C. by values from Landolt and Bornstein tables. All calculations were made by use of a seven-place logarithm table. Tammann's formula was used to find the vapor pressures, the formula $\mu = \frac{f - f''}{fC} \times 1000$, to find μ , and $M = \frac{0.18 Cf''}{f - f''}$ to find the molecular weight. Where f is

the vapor pressure of pure water, 27.76, as found by Lincoln and Klein; f ", the vapor pressure of the solution as found in these experiments; C , the concentration of the solution in grams solute per 100 grams water; and μ , 1000 times the relative lowering which one gram of the substance produces at the concentration C .

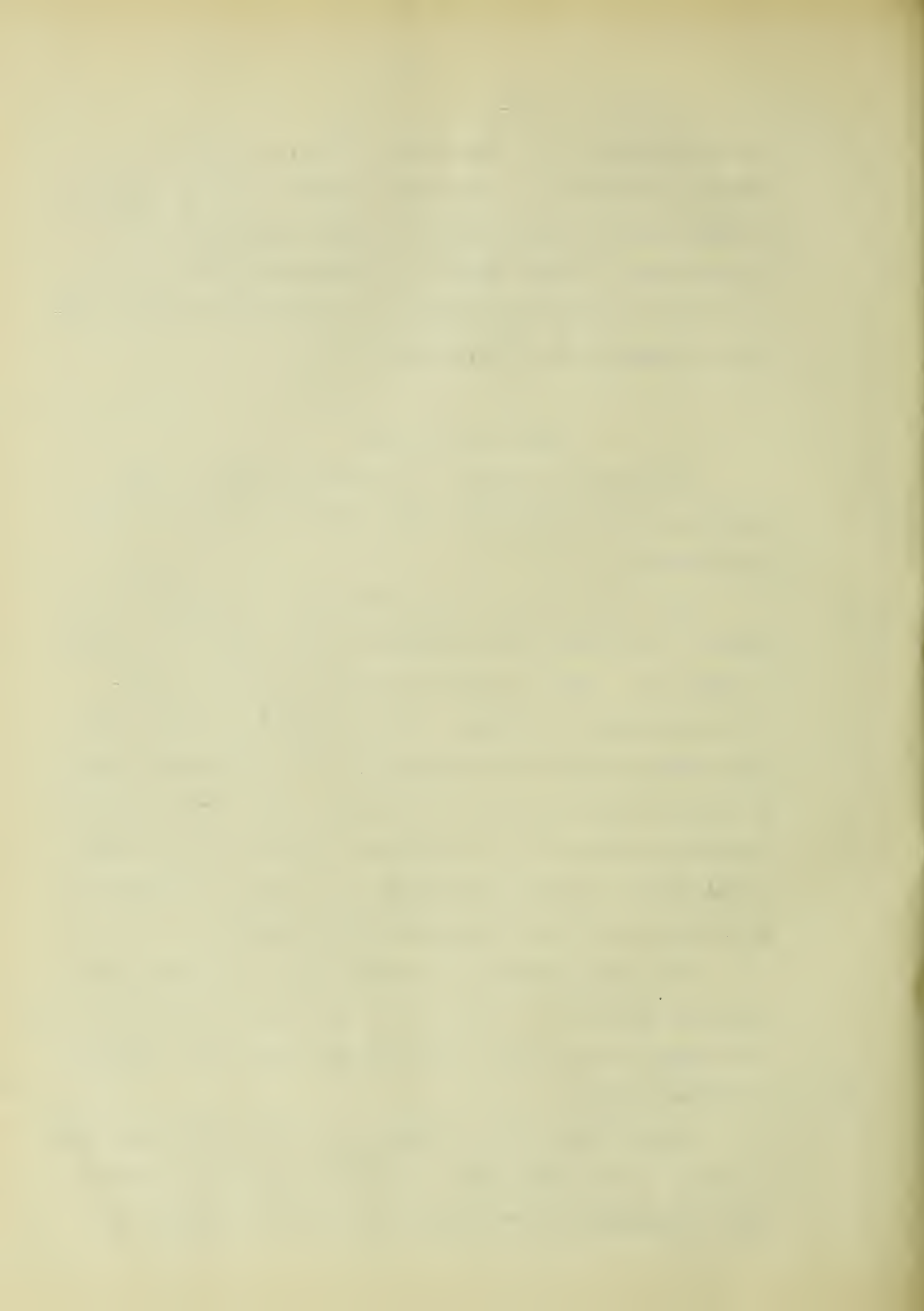
DATA AND RESULTS.

The data and results are shown in Table I. The headings of the columns have the same significance as in the formulae.

The values for μ and M obtained by Loomis⁽²¹⁾ and Jones⁽²²⁾ by means of the freezing point method, are shown in Table II. Their concentrations are given in gram-molecular normal solutions. Their highest concentration was a three times normal solution, while our lowest would be about a six times normal solution. Their results show a gradual increase of the molecular weight with increased concentration. Our results, likewise, show an increase in molecular weight with increased concentration.

The same agreement is shown again in the relation existing between the values of μ and the concentration. In both cases the molecular lowering decreases with increase of concentration.

Very little data on ammonium nitrate solutions could be found in the literature. The only data that could be used for comparison with ours being that of Loomis and



Jones, given above.

The accompanying curve was plotted with the concentrations as abscissae and the ratio $\frac{f - f''}{f}$ as ordinates. This curve shows the ratio to increase with the concentration.

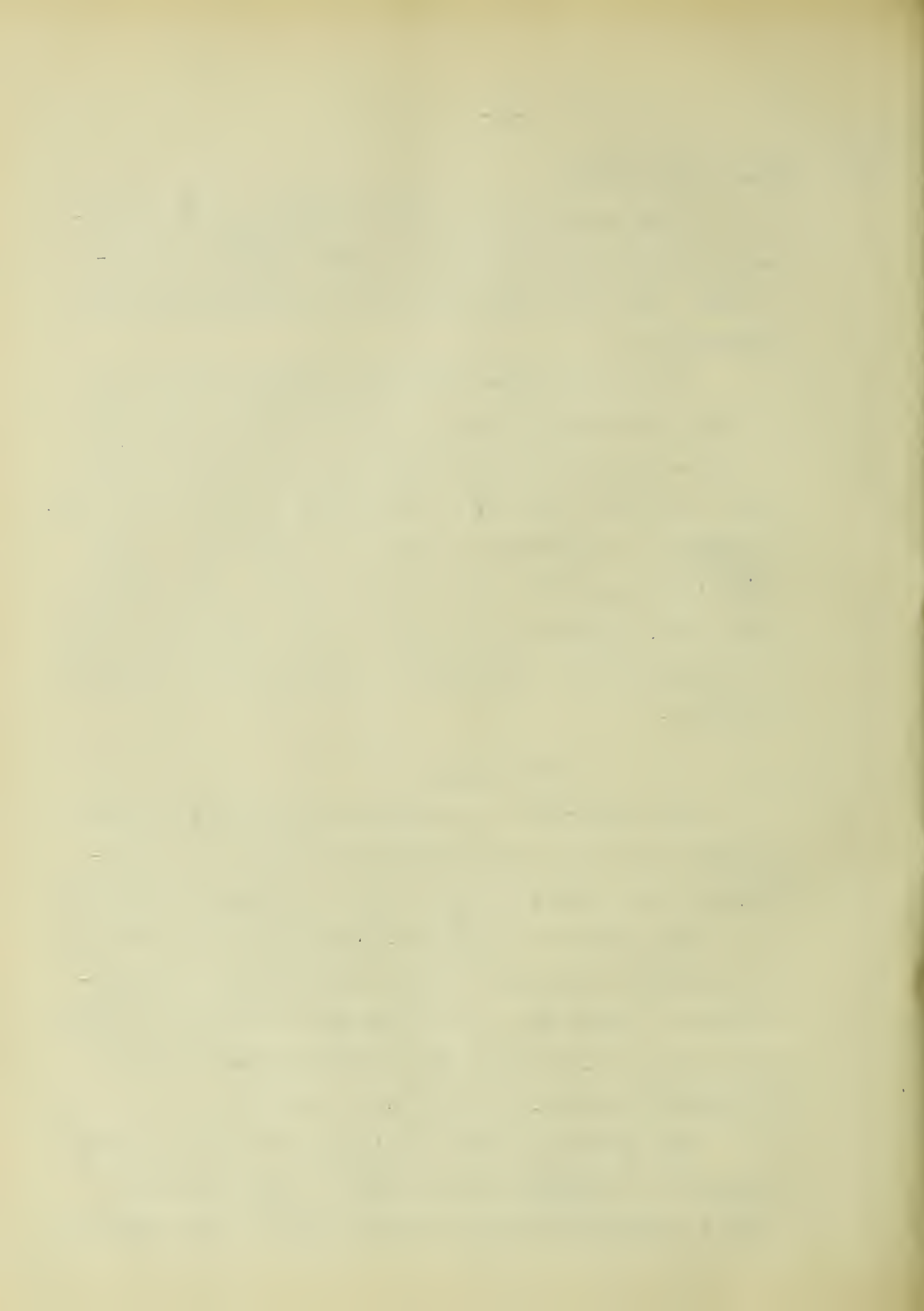
It has been stated that the molecular lowering of the vapor pressure of water by a set of salts of any acid is a function of the combining weight of the metal of the salt, the lower this weight, the greater the lowering. Then, if ammonium is considered a metal, it should give a molecular lowering greater than that for sodium. Our values show a less lowering as seen on the curve where the values for sodium nitrate are taken from determinations by Lincoln and Klein.

CONCLUSIONS.

This work taken in connection with that of Lincoln and Klein shows that the "saturation" method is a satisfactory method for determining vapor pressures of solutions.

The decrease in molecular lowering of the vapor and the increase in molecular weight with increase in concentration are exhibited in the solutions of ammonium nitrate used as in the freezing point determinations carried on by Loomis and Jones, in more dilute solutions.

The ammonium nitrate solutions give results of the same general character as the sodium nitrate solutions used by Lincoln and Klein, but the value for the molecular



lowering of the vapor pressure which should be greater according to theory, really is less than that of sodium nitrate.

Table I.

VAPOR PRESSURE OF AMMONIUM NITRATE SOLUTIONS.

C	H	V	t'	H-f'	P	f''	μ	M
184.64	731.32	32	25.33	708.79	.4663	15.207		
184.64	740.26	32	27.06	708.19	.4574	15.214		
					Mean	15.210	1.946	59.12
149.62	735.86	32	28.76	705.81	.4901	16.313		
149.62	735.04	32	29.20	705.03	.4894	16.314		
					Mean	16.314	2.094	57.66
112.90	736.10	32	28.52	706.82	.5228	17.344		
112.90	742.51	32	23.94	721.48	.5306	17.139		
					Mean	17.241	2.430	53.75
93.69	735.57	32	28.87	706.03	.5542	18.387		
93.69	734.14	32.82	22.79	714.39	.5826	18.219		
					Mean	18.303	2.451	56.65
48.98	731.76	32	25.84	705.85	.6258	20.393		
48.98	733.12	32	25.43	708.16	.6249	20.311		
					Mean	20.352	2.922	52.76

FREEZING POINT MEASUREMENTS ON AMMONIUM NITRATE.

Loomis		
m	$\frac{\Delta}{M}$	M
0.025	3.49	42.87
0.050	3.47	42.88
0.100	3.424	43.45
0.200	3.321	44.14
Jones.		
0.5	3.272	44.13
1.0	3.148	47.26
2.0	2.998	49.63
3.0	2.906	51.20

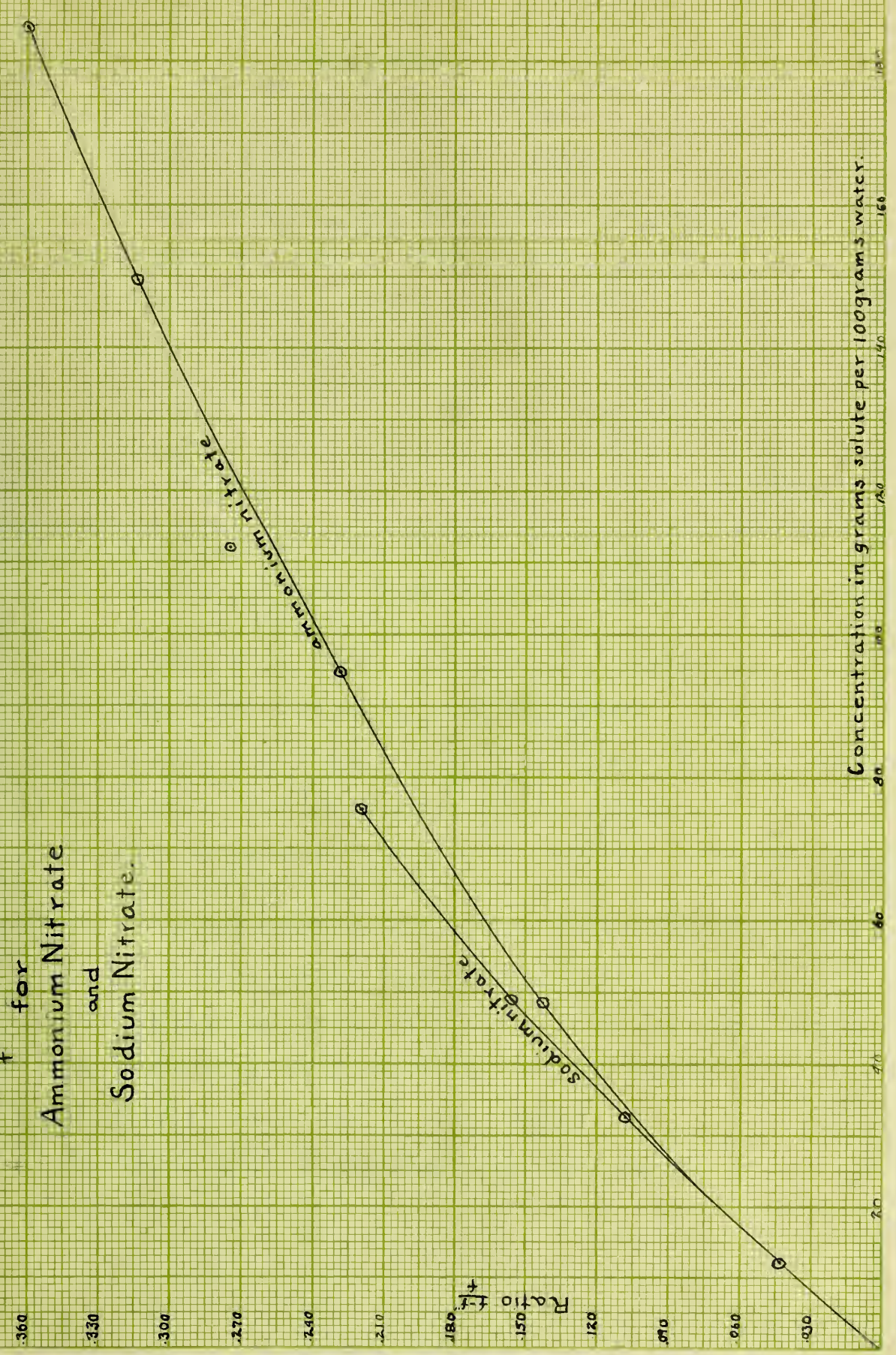
m = molecular concentration

$\frac{\Delta}{M}$ = molecular lowering.

M = molecular weight (calculated by us from data given.)

Curve Showing Relation of Ratio $\frac{f-f''}{f}$ to Concentration

for
Ammonium Nitrate
and
Sodium Nitrate.



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